Redox Potentials of M(VI)/M(V) Limiting Carbonate Complexes (M = U or Pu) at Different Ionic Strengths and Temperatures

Entropy and Heat Capacity.

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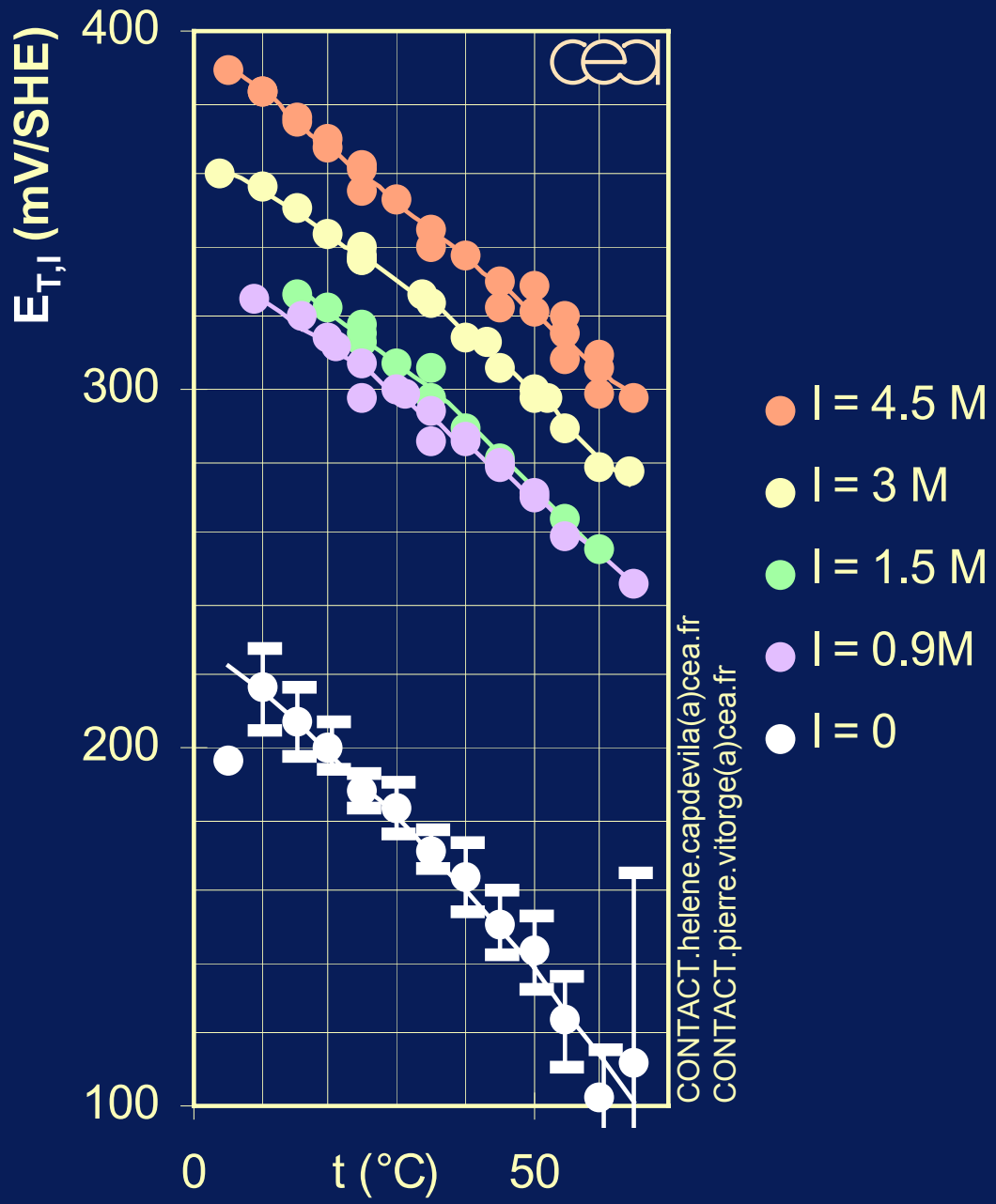
Temperature Influence on the Formal Potential of the $PuO_2(CO_3)_3^{4-}/PuO_2(CO_3)_3^{5-}$ Redox Couple



$$PuO_2(CO_3)_3^{4-} + e^- \rightarrow PuO_2(CO_3)_3^{5-}$$

$$E_{T,I} \approx E_{T°,I} + \Delta S_{T°,I} / F\,\Delta T + \Delta Cp_{T°,I} / (2\,F\,T°)\,\Delta T^2$$

Results (fitted parameters):

Na_2CO_3 (mol.l^{-1})	$E_{T°,I}$ (mV/SHE)	$\Delta S_{T°,I} / F$ (mV.K^{-1})	$\Delta Cp_{T°,I} / (2\,F\,T°)$ (μV.K^{-2})
0	**191 (8)**	**-1.84 (0.19)**	**-9.0 (6.5)**
0.3	306 (3)	-1.34 (0.09)	-3.8 (3.2)
0.5	315 (3)	-1.47 (0.13)	-7.7 (4.7)
1	338 (2)	-1.30 (0.04)	-8.7 (1.4)
1.5	360 (4)	-1.53 (0.07)	-8.4 (2.7)

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Data Treatment

$E_{T,I}$ Experimental Data

Data at I = 0

I Regression

T Regression

Modelling

$E_{(T,I)}\ F/(R\ T\ \ln 10) - 9\ D_{T,I} = E_{(T,0)}\ F/(R\ T\ \ln 10) - \Delta\varepsilon_T\ m_{Na^+}$

$E_{T,I} \approx E_{T°,I} + \Delta S_{T°,I} / F\ \Delta T + \Delta Cp_{T°,I} / (2\ F\ T°)\ \Delta T^2$

$E_{T,I} \approx E_{T°,0} + \Delta S_{T°,0} / F\ \Delta T + \Delta Cp_{T°,0} / (2\ F\ T°)\ \Delta T^2$

$\Delta\varepsilon_T \approx \Delta\varepsilon_{T°} + \Delta\varepsilon'_{T°}\ \Delta T + (\Delta\varepsilon''_{T°} / 2)\ \Delta T^2$

SIT formula for I corrections on E, ΔS, ΔCp and ΔH

$$E_{(T,I)} = E_{(T,0)} + (9\ D_{T,I} - \Delta\varepsilon_T\ m_{Na^+})\ R\ T\ \ln 10 / F$$

$$\Delta S_{T°,I} = \Delta S_{T°,0} + [9\ (D_{T°,I} + T°\ D'_{T°,I}) - (\Delta\varepsilon_{T°} + T°\ \Delta\varepsilon'_{T°})\ m_{Na^+}]\ R\ \ln 10$$

$$\Delta Cp_{T°,I} = \Delta Cp_{T°,0} + [9\ (2\ D'_{T°,I} + T°\ D''_{T°,I}) - (2\ \Delta\varepsilon'_{T°} + T°\ \Delta\varepsilon''_{T°})\ m_{Na^+}]\ R T°\ \ln 10$$

$$\Delta H_{T°,I} = \Delta H_{T°,0} + [9\ D'_{T°,I} - \Delta\varepsilon'_{T°}\ m_{Na^+}]\ R\ T°^2\ \ln 10$$

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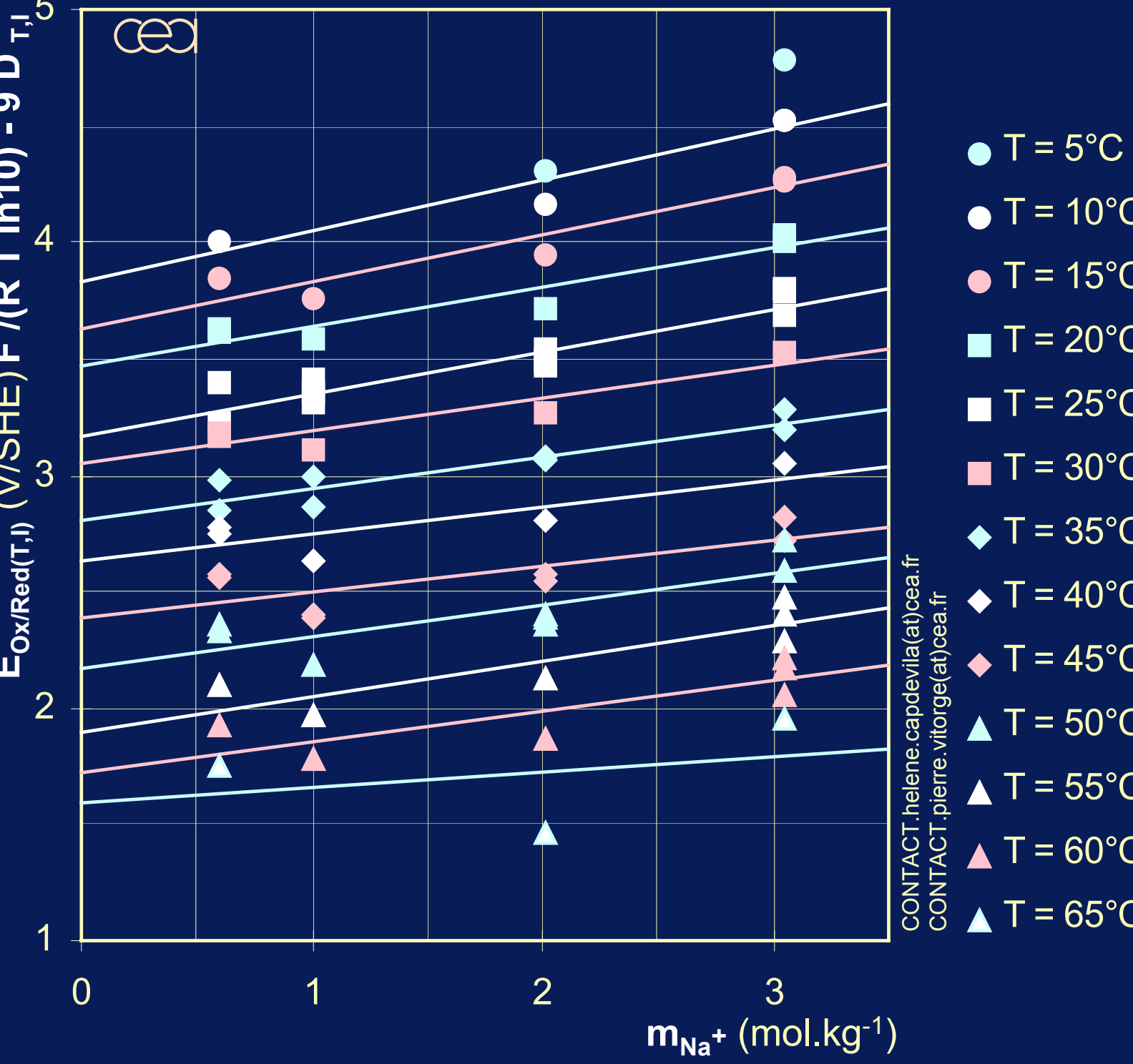
Ionic Strength Influence on the Formal Potential of the $PuO_2(CO_3)_3^{4-}/PuO_2(CO_3)_3^{5-}$ Redox Couple



$$PuO_2(CO_3)_3^{4-} + e^- \rightarrow PuO_2(CO_3)_3^{5-}$$

$$E_{Ox/Red(T,I)}\, F/(R\, T\, \ln 10) - 9\, D_{T,I} = E_{Ox/Red(T,0)}\, F/(R\, T\, \ln 10) - \Delta\varepsilon_T\, m_{Na^+}$$

$$D = a_T \sqrt{I} / (1 + b_T \sqrt{I}$$

$$E_{Ref(T,I)} = E_{Ag/AgCl(T,0)} + R\, T\, [\lg m_{Cl^-} - D_{T,I} + \varepsilon_{Na^+,Cl^-(T)}\, m_{Na^+}] / F$$

Results: $E_{Ox/Red(T,0)}$ and $\Delta\varepsilon_T$ fitted values

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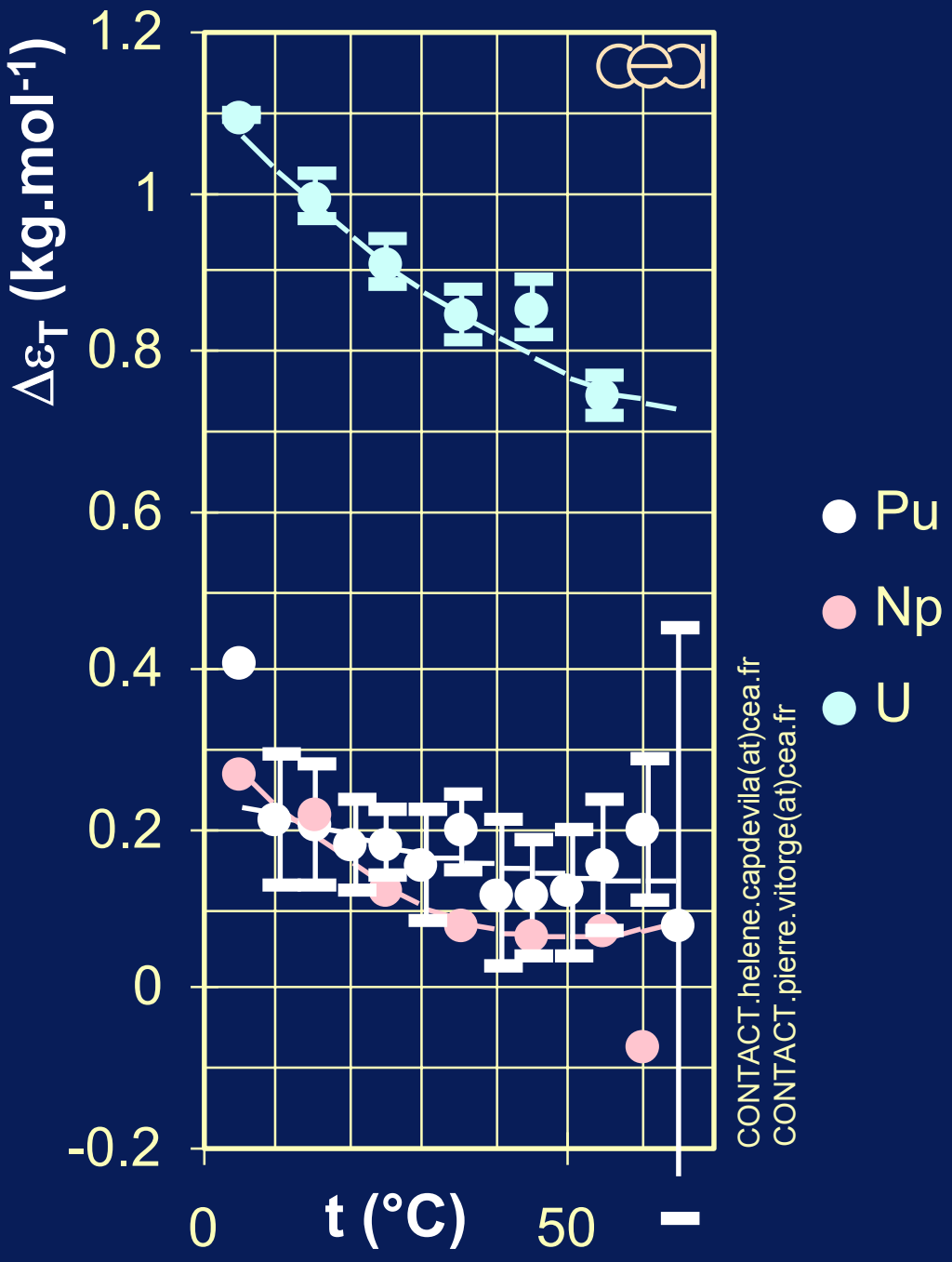
Temperature Influence on SIT Coefficient



$$PuO_2(CO_3)_3^{4-} + e^- \rightarrow PuO_2(CO_3)_3^{5-}$$

$$\Delta\varepsilon_T \approx \Delta\varepsilon_{T^\circ} + \Delta\varepsilon'_{T^\circ}\,\Delta T + (\Delta\varepsilon''_{T^\circ}/2)\,\Delta T^2$$

$$\Delta\varepsilon = \varepsilon_{PuO_2(CO_3)_3^{4-},Na^+} - \varepsilon_{PuO_2(CO_3)_3^{5-},Na^+}$$

$$E_{Ox/Red(T,I)}\,F/(R\,T) - 9\,D_{T,I} = E_{Ox/Red(T,I)}\,F/(R\,T) - \Delta\varepsilon_{T^\circ}\,m_{Na^+}$$

Results at T° for Pu:

$\Delta\varepsilon_{T^\circ} = 0.18_{(0.05)}$ kg.mol^{-1},
$\Delta\varepsilon'_{T^\circ} = -2.1_{(0.1)}$ g.mol^{-1}.K^{-1},
$\Delta\varepsilon''_{T^\circ} = 24$ mg.mol^{-1}.K^{-2}

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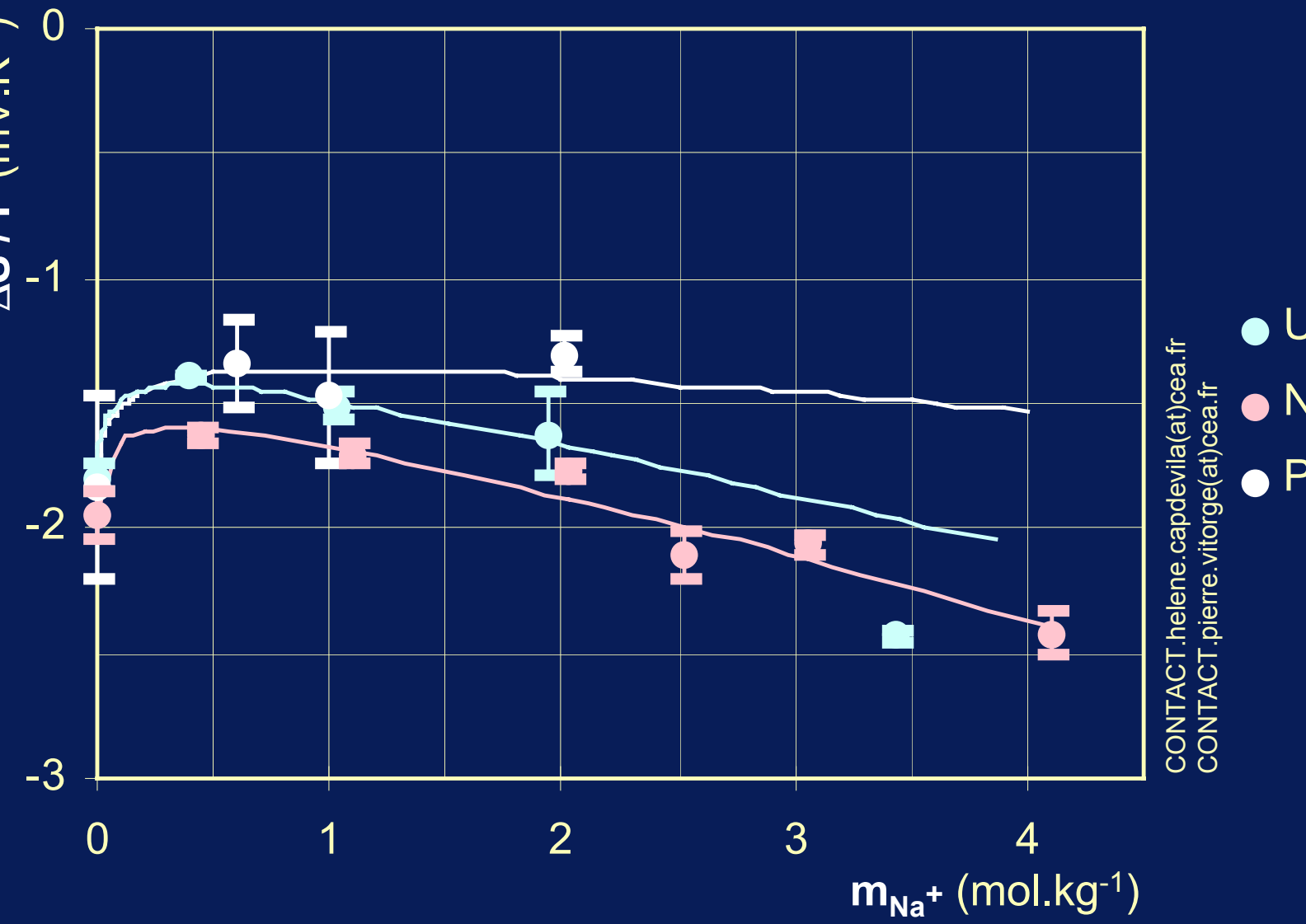
Ionic Strength Influence on Entropy



$$PuO_2(CO_3)_3^{4-} + e^- \rightarrow PuO_2(CO_3)_3^{5-}$$

$$\Delta S_{T^\circ,I} = \Delta S_{T^\circ,0} + [9\,(D_{T^\circ,I} + T^\circ\, D'_{T^\circ,I}) - (\Delta\varepsilon_{T^\circ} + T^\circ\, \Delta\varepsilon'_{T^\circ})\, m_{Na^+}]\, R\, \ln 10$$

$$E_{T,I} \approx E_{T^\circ,I} + \Delta S_{T^\circ,I} / F\, \Delta T + \Delta Cp_{T^\circ,I} / (2\, F\, T^\circ)\, \Delta T^2$$

Ionic Strength Influence on Enthalpy

$$\Delta H_{T^\circ,I} = \Delta H_{T^\circ,0} + [9\, D'_{T^\circ,I} - \Delta\varepsilon'_{T^\circ}\, m_{Na^+}]\, R\, T^{\circ 2}\, \ln 10$$

$$R\, \ln K_{T,I} \approx R\, \ln K_{T^\circ,I} - \Delta H_{T^\circ,I}\, \Delta(1/T) + T^{\circ 2} \Delta Cp_{T^\circ,I}/2\, \Delta\,(1/T)^2$$

$$\Delta G_{\ldots} = -R\, T\, \ln K_{\ldots} = -F\, E_{\ldots} \text{ or } \Delta G_{\ldots} = \Delta H_{\ldots} - T\, \Delta S_{\ldots}$$

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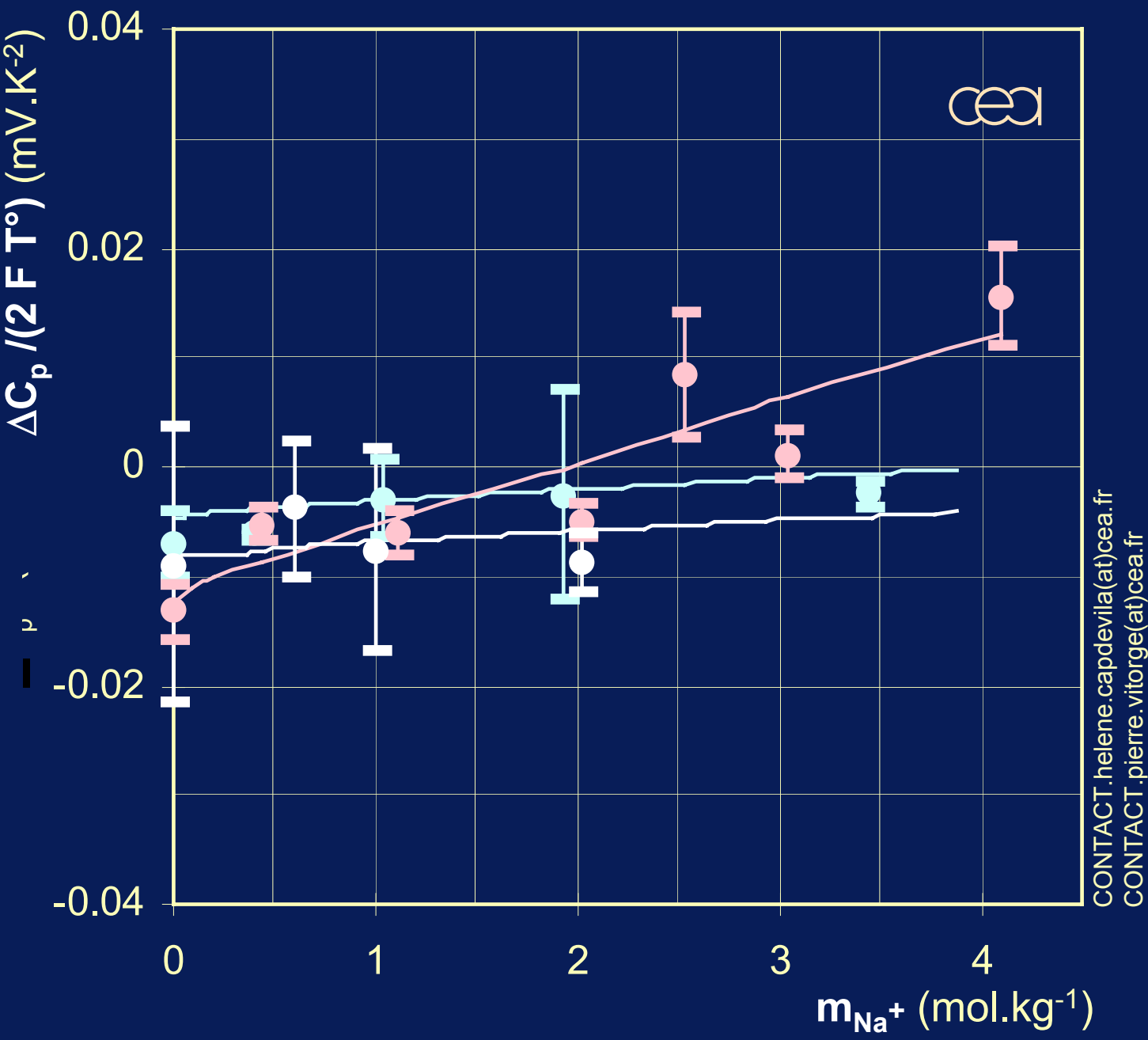
Ionic Strength Influence on Heat Capacity



$$PuO_2(CO_3)_3^{4-} + e^- \rightarrow PuO_2(CO_3)_3^{5-}$$

$$\Delta Cp_{T°,I} = \Delta Cp_{T°,0} + [9(2D'_{T°,I} + T° D''_{T°,I}) - (2\Delta\varepsilon'_{T°} + T°\Delta\varepsilon''_{T°})m_{Na^+}] RT° \ln 10$$

$$E_{T,I} \approx E_{T°,I} + \Delta S_{T°,I} / F \Delta T + \Delta Cp_{T°,I} / (2 F T°) \Delta T^2$$

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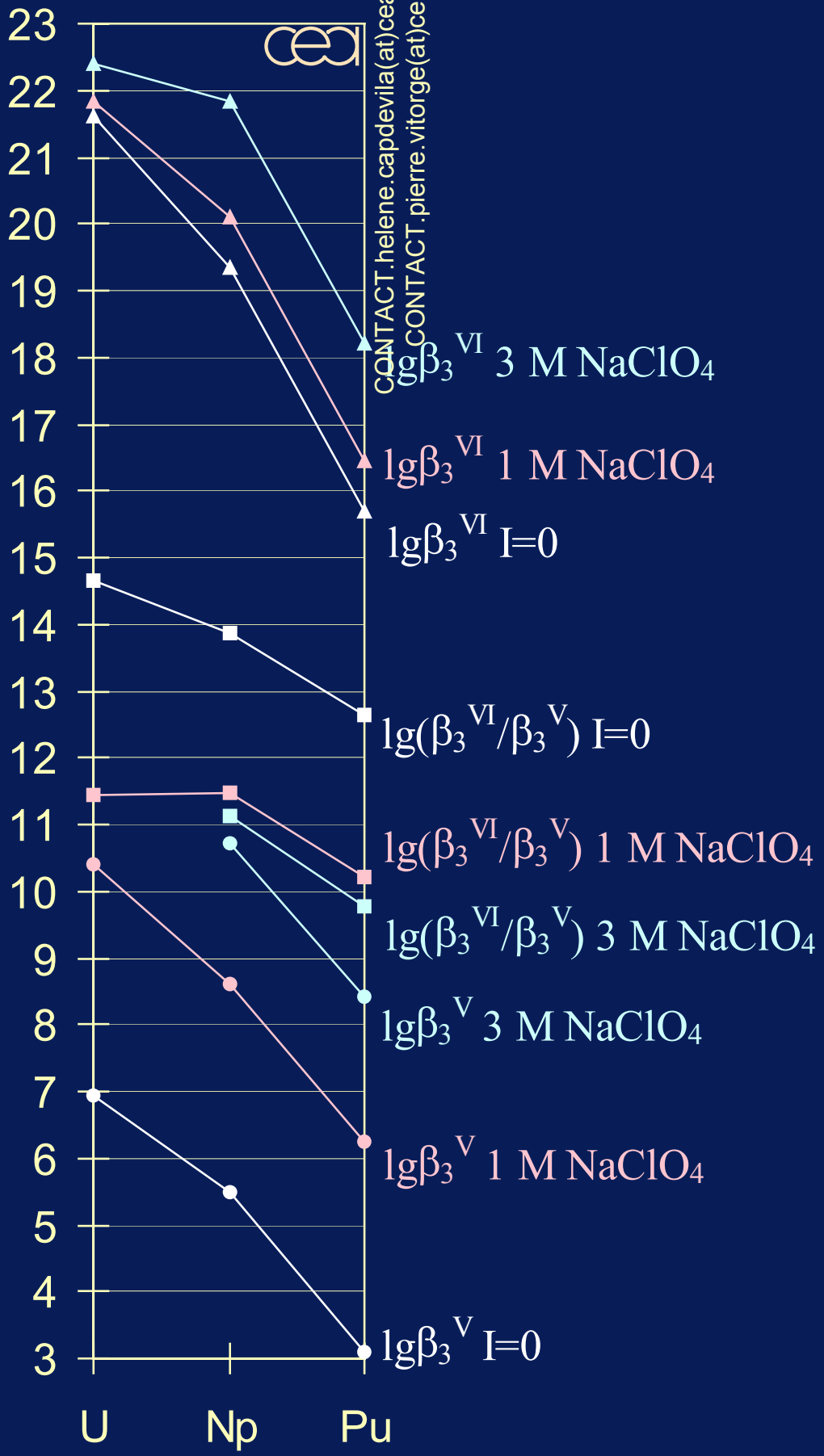
Formation Constants of Limiting Carbonate Complexes



$$\lg(\beta_3^{V}/\beta_3^{VI}) = (E_{Pu(VI)/Pu(V)} - E_{PuO_2^{2+}/PuO_2^{+}})F/(R\,T^\circ\,\ln 10)$$

$\beta_3^{VI \text{ or } V} = [PuO_2(CO_3)_3^{(4 \text{ or } 5)-}] / ([PuO_2^{(2 \text{ or } 1)+}]\,[CO_3^{2-}]^3)$